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Supplementary Materials for

Understanding deep ultraviolet surface enhanced Raman scattering: case study of Pt nanoparticles with modified Work Functions

Barbara Federica Scremin *et al.*

*Corresponding author. Email: scremin@iom.cnr.it. moreno.meneghetti@unipd.it

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Figs. S1 to S7

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1. DISC/NOL Chemical Science Department, University of Padova, Via Marzolo 1, 35131 Padova (Italy)
2. Physics Department, University of Trieste, Via Valerio, 2, 34127 Trieste, (Italy)
3. IOM-CNR, TASC Laboratory, Area Science Park Basovizza S.S. 14 km 163.5, 30149 Trieste

4 . Skolkovo Institute of Science and Technology, the territory of the Skolkovo Innovation Center, Bolshoy Boulevard, 30, p.1, Moscow 121205, Russia
5. Institute of Crystallography of Kurchatov Crystallography and Photonics Complex of NRC “Kurchatov Institute”, Academician Kurchatov Square, 1, Moscow, 123182, Russia
6. DiBio Imaging Facility, Dipartimento di Biologia, Università di Padova, Via U. Bassi 58/b, 35121 Padova (Italy)

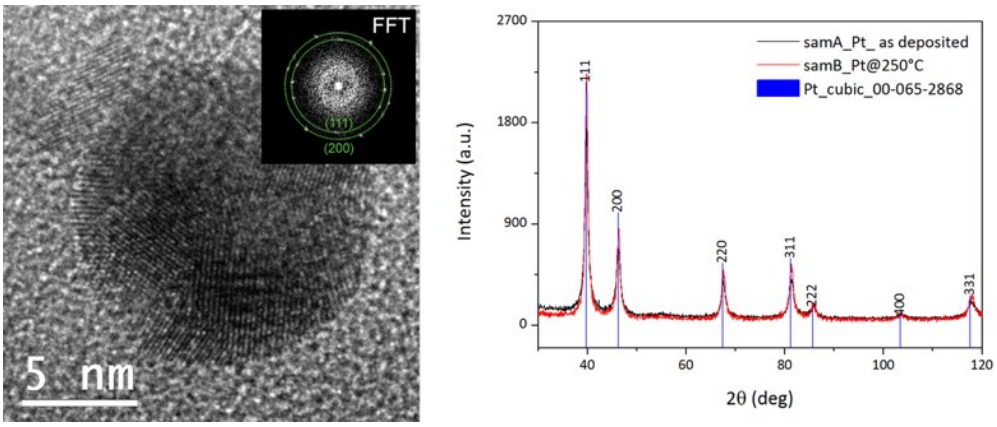

Fig. S1.

(Left side) HRTEM of a Pt NP, (right side) XRD of Pt NPs, showing a cubic fcc structure of the metal NPs.

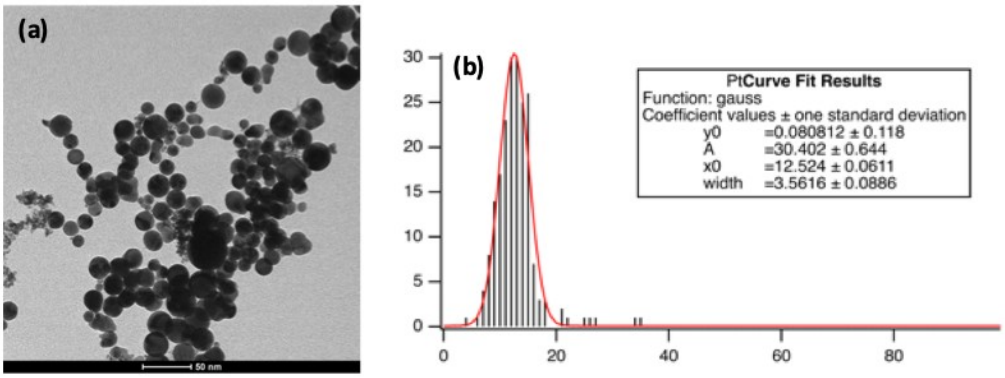

Fig. S2.

(A)TEM image of the $PtNP_{UPW}$ obtained in ultrapure water and quartz glassware; (B) size distribution and gaussian fitting.

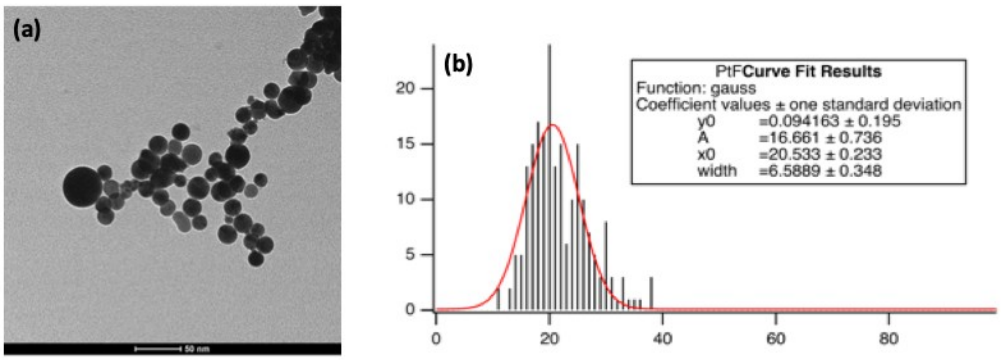

Fig. S3.

(A) TEM image of the $PtNP_F$ obtained by processing $PtNP_{UPW}$ with HF; (B) size distribution with gaussian fitting.

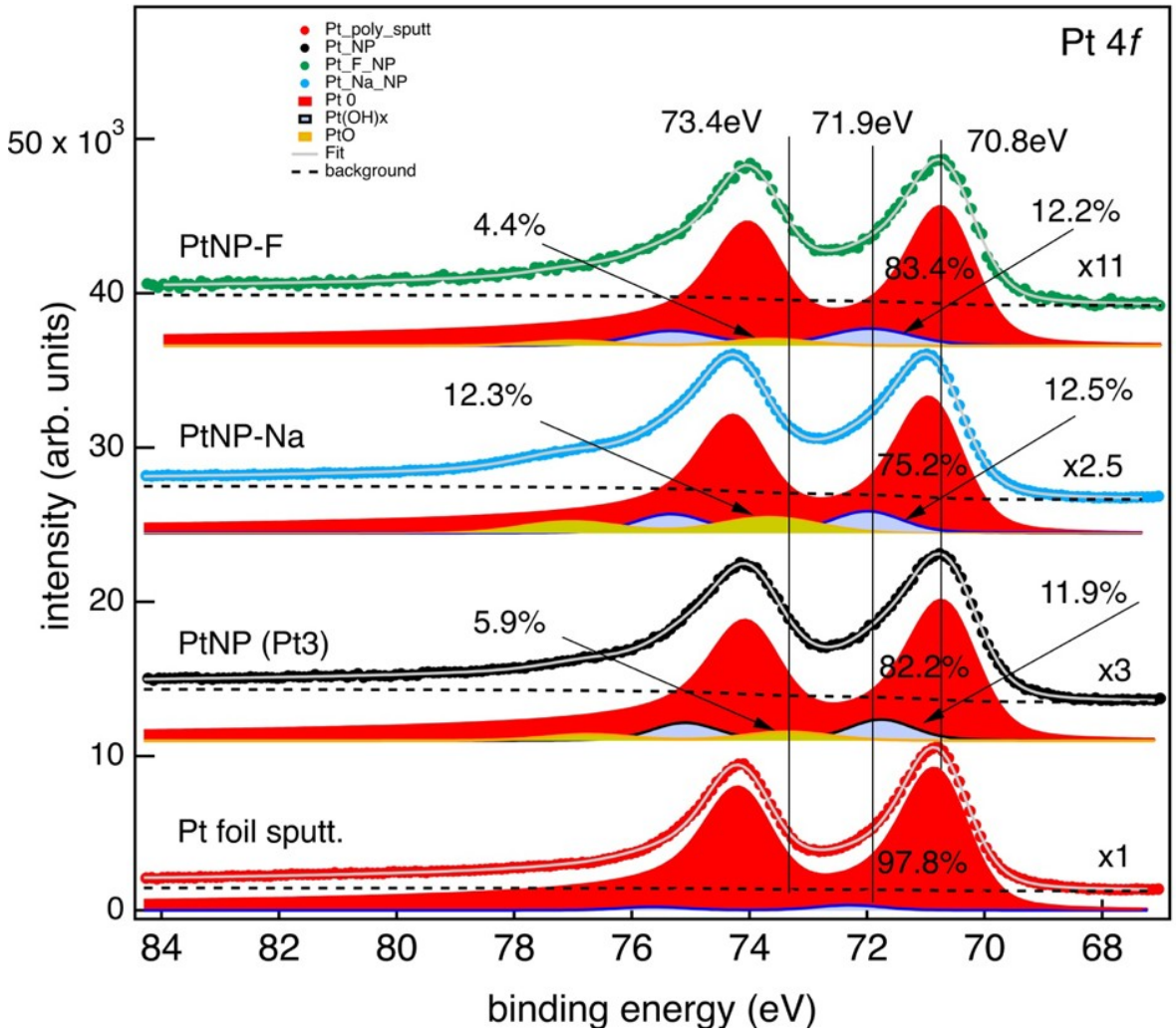
Pt_poly_sputt
Pt_NP
Pt_F_NP
Pt_Na_NP
Pt 0
Pt(OH)x
PtO
Fit
background
Pt 4f
73.4eV
71.9eV
70.8eV
50 x 10^3
PtNP-F
4.4%
83.4%
12.2%
x11
PtNP-Na
12.3%
75.2%
12.5%
x2.5
PtNP (Pt3)
5.9%
82.2%
11.9%
x3
Pt foil sputt.
97.8%
x1
intensity (arb. units)
binding energy (eV)
84
82
80
78
76
74
72
70
68
0
10
20
30
40

Fig. S4.

XPS, Pt4f core levels. Colours code: black: Pt-Na (WF 3.7 eV), blue: Pt (WF 5 eV), green: Pt-F (WF 5.8 eV), red: sputtered polycrystalline Pt (WF 4.7 eV, for reference). The chemical state of the as deposited NPs, and NPs after annealing in UHV at 250°C are analysed via XPS. Data indicate that a significant amount of platinum of the as deposited NPs is in metallic state, as shown both by the Pt 4*f* XPS core level (red component, Pt $4f_{7/2}$: 70.8eV, 82.2%) and by the presence of a metallic Fermi level in the valence band spectrum (Fig. 7, inset main text). XPS shows the presence of platinum in different oxidation states, which are compatible with Pt-$(OH)_x$ (blue component, Pt $4f_{7/2}$: 71.6eV-71.9eV, 11.9%) and Pt^{2+} (yellow component, Pt $4f_{7/2}$ at 73.4eV, 5.9%) (40-43). The presence of a stable platinum oxide explains the negative charging of the NPs evident in Z-Potentials performed in Na contaminated PtNPs in double distilled water of about (-30 ± 5.93) mV, suggesting the presence (44, 45) of species Pt-O like at the surface of the particles and the capture of oxides/hydroxides by the Pt surface, which explains the long-term stability of Pt NPs suspensions in water.

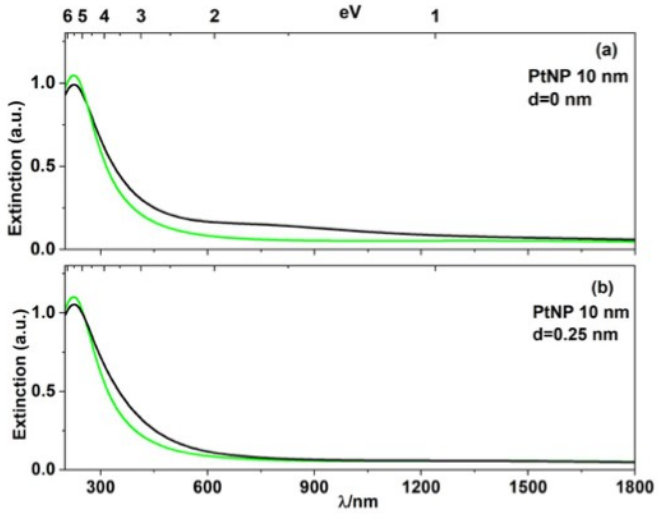

Fig. S5.

(A) Comparison of the extinction spectrum of a dimer of PtNP with particles of 10 nm size at the distance d = 0 nm (black line) and the spectrum of two isolated PtNP (green line) of 10 nm. (B) The same comparison, but with the distance of the particles in the dimer at d = 0.25 nm.

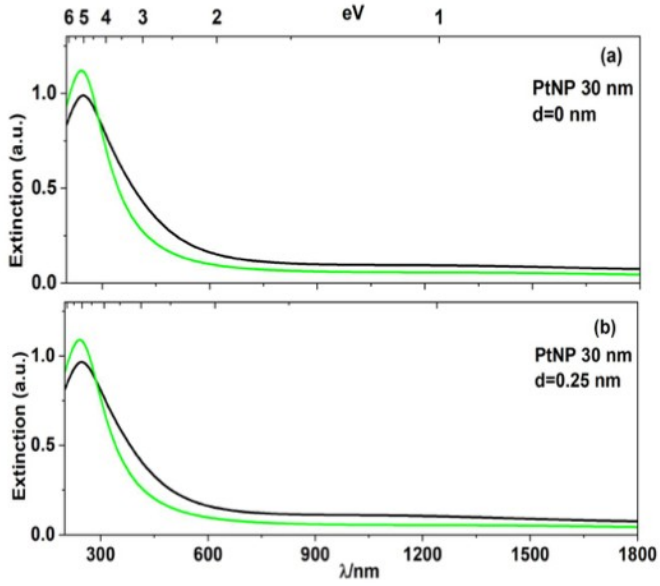

Fig. S6.
(A) Comparison of the extinction spectrum of a dimer of PtNP with particles of 30 nm size at the distance d = 0 nm (black line) and the spectrum of two isolated PtNP (green line) of 30 nm. (B) The same comparison, but with the distance of the particles in the dimer at d = 0.25 nm.

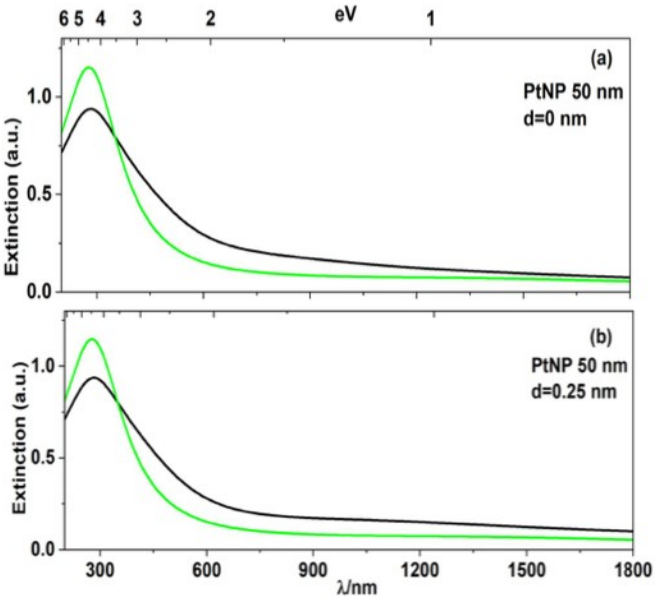

Fig. S7.
(A) Comparison of the extinction spectrum of a dimer of PtNP with particles of 50 nm size at the distance d = 0 nm (black line) and the spectrum of two isolated PtNP (green line) of 50 nm. (B) The same comparison, but with the distance of the particles in the dimer at d = 0.25 nm.